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Cyclopolymerization. IV. Low Molecular Weight Products for the Reactions of Allylamines and Diallylamines with Azobisisobutyronitrile

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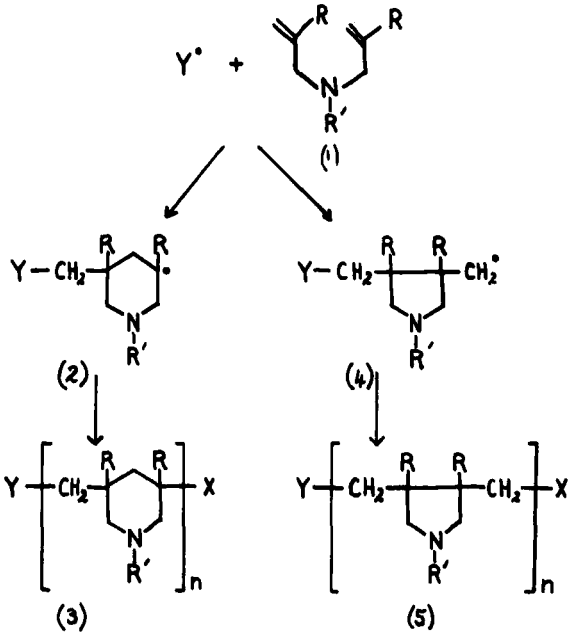
ABSTRACT

The azobisisobutyronitrile-initiated polymerization of various N-substituted diallylammonium, N-ethyldimethallylammonium, and triallylammonium chlorides yielded as the respective major by-products 2-substituted 6,6-dimethylperhydro-5-isoindolones, 2-ethyl-3a,6,6,7a-tetramethylperhydro-5-isoindolone, and 2-allyl-6,6-dimethylperhydro-5-isoindolone. These isoindolones are formed from pyrrolidylmethylene radical precursors and indicate that, in agreement with recent ESR studies, radical addition to diallylamines results in the formation of pyrrolidine derivatives and not piperidines as previously supposed. The reactions of azobisisobutyronitrile and azobisisobutyramidine dihydrochloride with the models, N,N-dimethylallylammonium and N,N,2-trimethylallylammonium chlorides, are also described.

INTRODUCTION

The radical-initiated polymerization of diallylamine and its derivatives (1) is commonly believed to proceed via the six-membered cyclic secondary radical (2) to yield poly(methylene-piperidines) (3) [1]. However, as reported in the previous papers [2, 3], the ESR spectra of the intermediate radicals were inconsistent with this hypothesis as the observed species corresponded to the thermodynamically less-stable primary radicals (4), suggesting that the poly(diallylamines) were in fact poly(dimethylenepyrrolidines) (5) (Scheme 1).

While the ESR studies have shown the presence of pyrrolidyl-methyl radicals (4), these species may not have been the principal reactive intermediates. It was therefore necessary to confirm the



Where a) R = H, R' = H
b) R = H, R' = CH_3
c) R = H, R' = $C(CH_3)_3$
d) R = H, R' = CH_2-C_6H_5
e) R = CH_3, R' = CH_2-CH_3
f) R = H, R' = CH_2-CH=CH_2

SCHEME 1.

ESR observations by the isolation and identification of products formed in typical radical-initiated cyclopolymerizations of diallylamines.

In this paper we describe the principal low-molecular weight products formed in the reactions of N-methyldiallylamine (1b) and the various diallylamine hydrochlorides (1a-1f, HCl) with cyanoisopropyl radicals generated by the thermolysis of azobisisobutyronitrile. We also describe the products of the reactions of cyano-isopropyl and amidino-isopropyl radicals with the model compounds, N,N-dimethylallylamine and N,N,2-trimethylallylamine hydrochlorides.

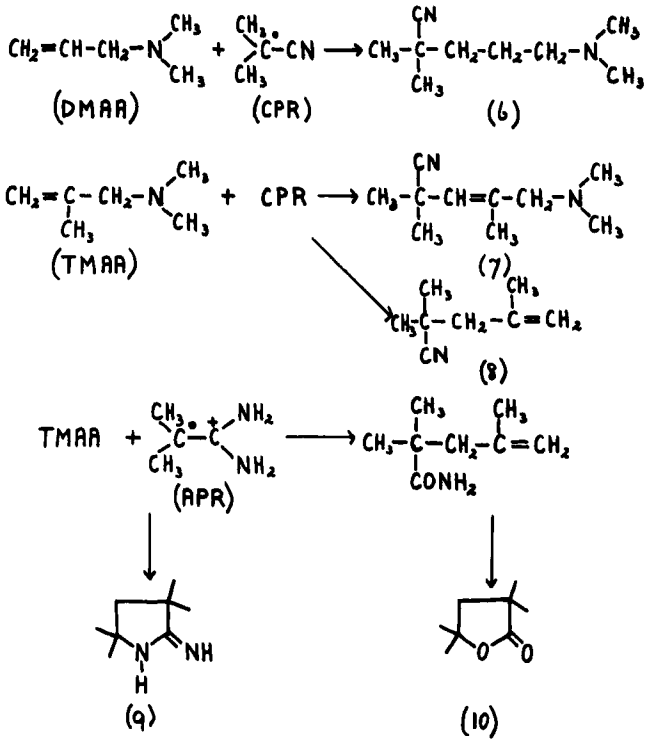
RESULTS AND DISCUSSION

A preliminary ESR investigation of the reactions of hydroxyl and amino radicals with N,N-dimethylallylamine (DMAA) and N,N,2-trimethylallylamine (TMAA) salts indicated that the predominant product species were formed by radical attack on the γ-carbon of the allyl or methallyl groups. This is in agreement with results reported by others for the corresponding reactions with allylamine and methallylamine salts [3-5]. The products formed (Scheme 2) when DMAA or TMAA salts react with cyanoisopropyl (CPR) or amidinoisopropyl (APR) radicals indicate that in these systems, too, attack occurs preferentially at the allylic γ-carbons. The intermediate radicals can react with further monomer molecules in a chain polymerization process, or terminate, either by gain of a hydrogen atom, as observed for the DMAA derivative (6) or, in the case of the TMAA derivatives, by loss of hydrogen (7) or a dimethylamino moiety (8).

As products formed by hydrogen transfer to monomer molecules were not detected, the TMAA derivatives presumably lost hydrogen by disproportionation with other radical species. The mechanism for elimination, or the fate of the dimethylamino fragment is unknown; dimethylamine was not detected in the reaction mixtures.

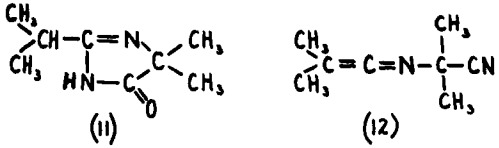
Although only stoichiometric quantities of hydrogen chloride were used in the reaction mixtures, the aqueous or ethanolic amine hydrochlorides dissociate sufficiently to catalyze various observed solvolytic reactions, such as the hydrolysis of amidinium groups to amides, nitrile groups to amides or esters, or the conversion of a hypothetical precursor (Scheme 2) to the lactone (10), the latter reaction proceeding readily in dilute acidic media [6].

The low reactivity of the DMAA and TMAA salts toward radical attack is reflected in the low conversion of the monomers, even when using relatively large amounts of initiator. The principal by-products of the reactions were tetramethylsuccinimide (TMSI) from azobisisobutyramidine dihydrochloride (ABIA), or isobutyronitrile (IBN),



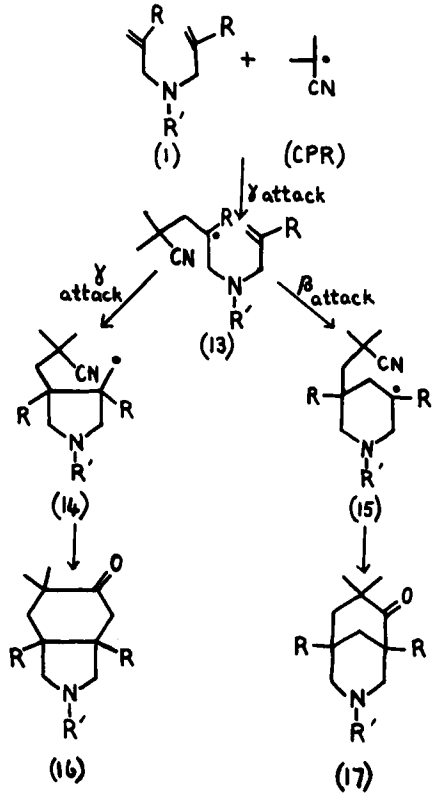
SCHEME 2.

ethyl isobutyrate (EIB), and tetramethylsuccinodinitrile (TMSN) from azobisisobutyronitrile (ABIB). Isobutyramide was also formed in these reactions, but was not assayed. 4,4-Dimethyl-2-isopropyl-2-imidazolin-5-one (DII) (11) was also obtained as a minor by-product from the ABIB systems, and was apparently formed by acid-catalyzed solvolysis and cyclization of the unstable ketenimine (12) in the ~2 N ethanolic amine salt media. The imidazolinone (11) was not found, however, among the small quantity of basic products formed in the decomposition of ABIB in 2 N ethanolic hydrogen chloride.

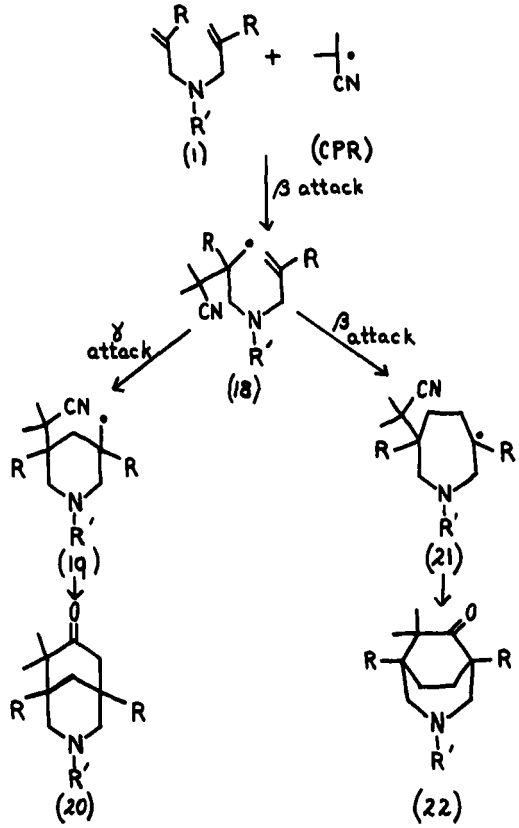


In the reactions of ABIB with the various ethanolic amine hydrochlorides (1a-1f, HCl), up to half the ABIB was recovered as the by-products isobutyronitrile, ethyl isobutyrate, and tetramethylsuccinodinitrile, again reflecting the low reactivity of the diallylamines toward attack by CPR. The basic products from these reactions included the poly(diallylamines) which will be discussed in a subsequent paper, the imidazolinone (11), and as major by-products, volatile aminoketones, derivatives of 6,6-dimethylperhydro-5-isoindolone (16).

The aminoketone formed in the N-methyldiallylamine (MDAA, 1b)-ABIB reaction had the molecular formula $C_{11}H_{19}NO$, and its IR and ^{1}H-NMR spectra indicated a saturated bicyclic structure containing a cyclohexanone ring, and $CH_3N(CH_2-)_2$ and $(CH_3)_2C$ groups. It appeared that the aminoketone was formed in a "backbiting" reaction of a CPR-MDAA adduct-radical, e.g., (14), and that four structures were possible, depending on whether the initial reaction with CPR and the subsequent cyclization of the MDAA involved attack at the β-carbons and/or γ-carbons of the allylic groups (Schemes 3 and 4, where R and R' are as in Scheme 1).



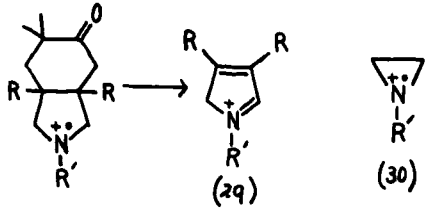
SCHEME 3.



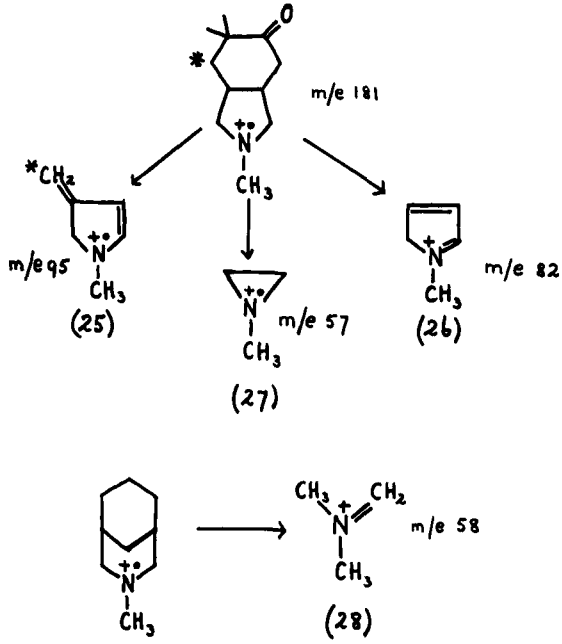
SCHEME 4.

The presence of two exchangeable protons and the formation of an α-oximino derivative indicated structure (16) or (20). The complexity of the ^{1}H-NMR spectra of the aminoketone and its Wolff-Kischner reduction product prevented a facile differentiation between the possible structures, although the ^{13}C-NMR spectra supported the structure (16b) and eliminated the most-likely alternative structure (17b). Dr. S. R. Johns of this Division has analyzed the ^{13}C-NMR spectra of the compounds (16b), (16c), and (23b); these will be discussed in a following paper [7].

The structure of the aminoketone was deduced from its mass spectrum. Fragmentation of the aminoketone and the deuterated aminoketone largely involved the cyclohexanone ring and the



$-C(CH_3)_2.CO.CH_2$-group, and resulted in the formation of the methylene-pyrroline radical-cation (25), m/e 95, and the pyrroline cation (26), m/e 82, as prominent ions which were unaffected by the deuterium exchange. The most abundant ion observed in the spectra of (27b) and (23b) was the N-methylaziridine radical-cation (27), m/e 57, whereas 3-methyl-3-azabicyclo[3,3,1] nonane derivatives have been shown to form the dimethylmethylenimonium cation (28), m/e 58, as the base ion by a process involving hydrogen-abstraction from the bridging methylene group [8], (Scheme 5).



SCHEME 5.

The configuration of the perhydroisoindole ring junction of compound (23b) has been examined using lanthanide-induced ^{13}C-NMR chemical shifts, but initially with ambiguous results [7]. However, consideration of the lack of reactivity of the keto-methylene group of (16b) suggested the cis-configuration, as examination of Drieding models showed that the methylene group in this structure probably would be shielded by the N-methyl and one of the geminal C-methyl groups. 2,5,5-Trimethyl-cis-perhydroisoindole was synthesized from 5,5-dimethyl-4-keto-cyclohexane-cis-1,2-dicarboxylic acid by standard procedures, and was found to be spectroscopically and chemically identical with the amine (23b). As ring-junction isomerization during the Wolff-Kischner reduction was unlikely, the aminoketone formed in the MDAA-ABIB reaction was established as 2,6,6-trimethyl-cis-perhydro-5-isoindolone (16b). Synthesis of the trans-isomers of the amine and the aminoketone are at present in hand.

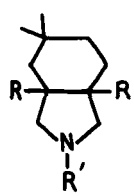
The structures of the other aminoketones (16e, 16f), formed, respectively, from the diallylamines (1c-1e) and triallylamine (1f), were deduced from the marked similarities in basic features in their IR and in their NMR spectra. In particular, the similarity between the ^{13}C-NMR spectra of (16b) and (16c) suggested that the aminoketone derived from n-tert-butyldiallylamine (1c) was 2-tert-butyl-6,6-dimethyl-cis-perhydro-5-isoindolone. N-Benzyldiallylamine (1d) and triallylamine (1f) yielded 2-benzyl- (16d) and 2-allyl-6,6-dimethylperhydro-5-isoindolone (16f), respectively.

Diallylamine (1a) and N-ethyldimethallylamine (EtDMA) (1e), in contrast to the other systems, yielded significant amounts of other volatile basic products in addition to the expected aminoketones.

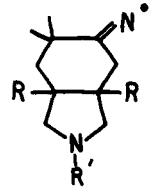
Results from studies on analogous 1,6-diene and related systems [9, 10] suggested that there would be a much greater probability of the CPR-EtDMA intermediate radical having the piperidine structure (15e). However, the principal component of the aminoketone fraction contained two exchangeable protons and its mass spectrum indicated that it was 2-ethyl-3a,6,6,7a-tetramethylperhydro-5-isoindolone (16e) and not the alternative structure (17e). The diallylamine reaction was anomalous, and will be reported at a later date.

The mass spectrum of each of the aminoketones was distinctive, but common features were: prominent $(M-1)^+$, and also $(M-2)^+$ and $(M-4)^+$ formed by dehydrogenation in the heated inlet of the spectrometer; $(M-CH_3)$, $(M-H_2O)$, $(M-CO)$, and $(M-CH_2CO)$ ionic species; prominent pyrroline cations (29) which retained the bridgehead substituents; and the substituted aziridine cations (30). In the case of the N-tert-butyl, N-ethyl, or N-allyl derivatives, prominent ions were also formed by the loss of the elements of CH_3 or C_2H_3 from the N-substituent group.

Although the 6,6-dimethylperhydro-5-isoindolones (16) were the predominant low-molecular weight basic products formed in the reactions between the various diallylamines and ABIB, there were also



(23)



(24)

present small, sometimes negligible, amounts of other unidentified basic products, and it is possible that these include piperidines or acyclic species, particularly in the case of the EtDMA-ABIB system. However, the predominant reaction between CPR and the various diallylamines appears to consist of a slow attack of the radical at an allylic γ-carbon (13), followed by a rapid and irreversible cyclization to the corresponding pyrrolidylmethyl radical (14), capable of propagating a chain polymerization reaction. The radical (14) could either abstract a hydrogen atom from the solvent, or combine or disproportionate with another radical species, neither of which occurs to an appreciable extent.

Alternatively, the radical (14) could undergo an intramolecular attack on the cyano group to yield the imino radical (24). Such reactions are uncommon, although the intramolecular cyclization of acrylonitrile macroradicals is a well-known secondary reaction occurring during polymerization [11]. A. L. J. Beckwith has also recently observed ESR signals corresponding to imino radicals formed by the intramolecular cyclization of o-cyanophenylethyl and o-cyanophenoxymethyl radicals [12]. The imino radical (24) could abstract hydrogen from the solvent or other species, forming the ketimine (24b) which would be rapidly hydrolyzed in the acidic reaction media. A volatile, hydrolyzable precursor to the aminoketone was observed on GLC analysis of products from the reaction of MDAA base and ABIB in dry benzene. Although the putative imino radical could initiate polymerization of MDAA, this apparently does not occur as the yield of aminoketone after hydrolysis corresponded to the apparent yield of the volatile precursor, as measured by comparison of the areas under the respective GLC peaks. The formation of (16b) also occurs in the reaction between MDAA base and ABIB in ethanol, or in the presence of di-n-butyl disulfide. Intramolecular cyclization of the radical (14) appears to be a rapid reaction, and competitive with the propagation reaction with additional diallylamine molecules. Once the polymerization has commenced, however, intramolecular cyclization would cease to be an effective termination process for the polymer radical.

The possibility that the piperidyl radicals (2) might be the principal reactive species in propagation of the chain polymerization

reaction is unlikely in the systems discussed in this paper, with the possible exception of EtDMA, as no significant amounts of low molecular weight piperidines were detected in the reaction products. The low average molecular weight of the polymer formed, and the low conversion of the monomer precludes the alternative explanation that the rate of propagation of the hypothetical piperidyl radical (2) was sufficiently greater than the rates of the various termination reactions to account for the absence of low molecular weight piperidines.

Details of the polymer structures and the nature of the end groups will be discussed in a subsequent paper, as will the reaction between the diallylamines and phenyl, methyl, benzoyl, and hydroxyl radicals. However, ^{1}H and ^{13}C NMR spectra of the ABIB-initiated N-methyldiallylamine polymer are consistent with a saturated poly(3,4-dimethylene-1-methylpyrrolidine) structure (5b).

Although the work reported in this paper mainly considered the reactions of CPR with diallylamines, ESR studies suggest that the structure of the cyclic intermediate radicals is not sensitive to the nature of the initiating species. Brace [13] has also shown that the radical-induced reactions of certain diallylamines with 1-iodoperfluorobutane yield the corresponding 3-iodomethyl-4-(nonafluoropentyl)pyrrolidines, indicative of pyrrolidylmethyl radical intermediates.

The structures of the low molecular weight products obtained from the reaction of cyano-isopropyl radicals with various diallylamine derivatives indicate that the predominant reactive intermediate species are pyrrolidylmethyl radicals, in agreement with the ESR results, and not piperidyl radicals as much of the previously published work would suggest. It is probable that this conclusion is true for the reaction of these diallylamines with other initiator radicals, and in consequence, that the polymers formed will consist predominately of dimethylenepyrrolidine units.

EXPERIMENTAL

Reagents and Methods

The amines were either purified commercial specimens or were synthesized using standard procedures. 2,2-Azobisisobutyronitrile (ABIB), Fluka pure-reagent grade, was used as received. 2,2-Azobisisobutyramidine dihydrochloride (ABIA) was prepared by the method of Dekking [14]. Gas chromatographic (GLC) analyses and fractionation of the volatile reaction products were performed using SE-30 and APL-coated stationary phases. Proton NMR spectra were measured at 60 and 100 MHz in $CDCl_3$ solutions with

TMS as an internal reference. Infrared spectra were measured in KBr disks or as thin films. Mass spectra were measured with a Hitachi-Perkin-Elmer RMU-6D spectrometer using heated-inlet sampling at 200°C and 70 eV ionisation potential. Microanalyses were performed by the Australian Microanalytical Service.

(a) Reaction of N,N-Dimethylallylamine (DMAA) with ABIB

DMAA (9.5 g, 112 mmoles), HCl (4.2 g, 112 mmoles), ABIB (9.2 g, 56 mmoles), and ethanol (50 ml) were heated together at 60°C under reflux in a N_2 atmosphere for 72 hr. The bulk of the solvent was then removed by distillation, the residue diluted with water, and then extracted with diethyl ether to remove the neutral products. The aqueous phase was treated with NaOH and the liberated bases extracted with ether and with chloroform. The aqueous residue was neutralized with CO_2, evaporated, and then extracted with a small quantity of ethanol. Each fraction was examined using quantitative gas and thin-layer chromatography.

The ethanolic distillate and neutral fraction contained isobutyronitrile (IBN, 5 mmoles), ethyl isobutyrate (EIB, 11 mmoles), and tetramethylsuccinodinitrile (TMSN, 32 mmoles), together with several minor, unidentified components; the IBN, EIB, and TMSN were each identified by comparison with authentic specimens. The basic fraction contained unchanged DMAA (~70 mmoles), and on distillation yielded a fraction, bp 70-100°C/1 mm (1.8 g), and a high-boiling residue (2.2 g). There was no evidence of free methacrylonitrile or of simple products formed by hydrogen-abstraction from the solvent. The volatile basic fraction contained numerous components, but the major component was separated by preparative GLC and identified as 2,2-dimethyl-5-dimethylaminovaleronitrile (6); mass spectrum: M^+, m/e 154 (intensity 14), 84 (6), 82 (1), 71 (2), 70 (2), 68 (2), 67 (1), 58 (100), 44 (7), and 42 (17); infrared: C≡N, 2250 cm^{-1}; NMR: $N(CH_3)_2$, δ 2.22; $C(CH_3)_2$, δ 1.35; picrate, mp, 126°C. Analysis: calculated for $C_{15}H_{21}N_5O_7$: C, 47.0; H, 5.5; N, 18.3; found: C, 47.3; H, 5.6; N, 18.1.

(b) Reaction of N,N-Dimethylallylamine (DMAA) with ABIA

DMAA (4.3 g, 50 mmoles), 10.5 M hydrochloric acid (4.7 ml, 49 mmoles), ABIA (1.37 g, 5 mmoles), and water (5 ml) were heated together and the resultant mixture analysed as described for Reaction (a) above. The products included tetramethylsuccinimide (TMSI) (1.8 mmoles), unchanged DMAA (33 mmoles), and high-boiling basic

residue (0.3 g). The TMSI, mp, 187°C (Ref. 15, 188°C), was identified by its mass spectrum: M^+ m/e 155 (intensity 41), 84 (100) 69 (71), and 41 (30); IR: C=O, 1792 cm^{-1}. The high-boiling and aqueous residues contained a mixture of amino-amides (C=O, ~1690 cm^{-1}). There was no evidence for amidine-substituted products, and the aqueous residue contained NH_4Cl presumably formed by hydrolysis of the amidine groups.

(c) Reaction of N,N,2-Trimethylallylamine (TMAA) with ABIB

TMAA (6.9 g, 68 mmoles), HCl (2.4 g, 64 mmoles), ABIB (5.6 g, 34 mmoles), and ethanol (30 ml) were treated as described for Reaction (a). The neutral fractions contained IBN (4.7 mmoles) and EIB (5.8 mmoles), TMSN (15 mmoles), and a small amount of 2,2,4-trimethylpent-4-enenitrile, described below. The basic fraction contained unchanged TMAA (42 mmoles), and on distillation yielded fractions (i) bp, 120°C/20 mm (0.6 g); (ii) bp, 110-120°C/0.1 mm (0.8 g); and a high-boiling residue (0.3 g). The 2,2,4-trimethylpent-4-enenitrile (8) was separated by preparative GLC and identified by its IR spectrum (C≡N, 2270 cm^{-1}; C=C, 910 cm^{-1}) and mass spectrum: M^+ m/e 123 (intensity 45), 122 (13), 105 (43), 81 (23), and 55 (100). Calculated for $C_8H_{13}N$: M^+, m/e 123; $M+1^+/M^+$, 0.092; $M+2^+/M^+$, 0.004; found: $M+1^+/M^+$, 0.090; $M+2^+/M^+$, 0.005.

The basic fraction (i) was purified by preparative GLC and identified as 5-dimethylamino-2,2,4-trimethylpent-3-enonitrile; mass spectrum: M^+, m/e 166 (intensity 3), 122 (1), 108 (1), 98 (5), 96 (3), 83 (3), 69 (4), 58 (100), 56 (6), 44 (18), and 42 (26); NMR spectrum: $(CH_3)_2N$, δ2.18; C=C−CH_3, δ2.34; CH_2N, δ2.94; C=CH, δ3.06, 3.13; IR: 2270, 1630, 920, 850 cm^{-1}. Fraction (ii) contained a crystalline component, mp, 104°C, which was sparingly soluble in ether; the remainder of the fraction, which is still under investigation, consisted of a mixture of nitrile and amide-substituted amines. The crystalline component was identified as 4,4-dimethyl-2-isopropyl-5-imidazoline (11, DII), or its tautomer. Calculated for $C_8H_{14}N_2O$: C, 62.3, H, 9.2; N, 18.2; found: C, 62.7; H, 9.3; N, 18.1; IR: 3400, 1655, 1553 cm^{-1}; NMR spectrum: $(CH_3)_2CH$, 6-H doublet, δ1.16; 1-H multiplet, δ2.40; $(CH_3)_2C$, 6-H singlet, δ1.72; mass spectrum: M^+, m/e 154 (intensity 35), 139 (4), 127 (7), 111 (27), 100 (8), 84 (12), 71 (86), 68 (95), 58 (20), 57 (18), 43 (100), 42 (27), and 41 (39).

(d) Reaction of N,N,2-Trimethylallylamine (TMAA) with ABIA

A mixture of TMAA (5.0 g, 51 mmoles), 10.5 M hydrochloric acid (4.7 ml, 49 mmoles), ABIA (5.4 g, 20 mmoles), and water (5 ml) was

treated as described for Reaction (a). The neutral fraction yielded TMSI (4.7 mmoles) and 2,2,4,4-tetramethyl-N-butyrolactone (10, 6 mg). The basic fraction contained unchanged TMAA (34 mmoles) and on molecular distillation at 100-120°C/0.01 mm yielded a mixture of amino-amides (1.4 g), which is still under investigation, and a high-boiling residue (0.9 g). Repetition of the reaction using TMAA.HCl (50 mmoles) and ABIA (5 mmoles) yielded TMSI (1.7 mmoles), the lactone (1.1 mmoles), unchanged TMAA (40 mmoles), and 2 high-boiling residue (0.35 g), which on treatment with diethyl ether yielded sparingly-soluble crystals (50 mg), recrystallized mp, 154-156°C. In both reactions the aqueous waste contained ammonium chloride and unidentified amino-amides. The 2,2,4,4-tetramethyl-butyrolactone, mp, 39°C (Ref. 6, 41-42°C) was identified by its spectra: NMR 6-H singlets, δ 1.34, 1.47; 2-H singlet, δ 2.05; IR: C=O, 1770 cm^{-1}; M^+, m/e 142 (intensity 0.3), 141 (0.3), 127 (45), 98 (40), 83 (100), 56 (60), 55 (65), and 43 (90). Calculated for $C_{18}H_{14}O_2$: C, 67.6; H, 9.9; found: C, 67.9; H, 9.9. The material mp, 154-156°C, was tentatively assigned as 5-imino-2,2,4,4-tetramethyl-pyrrolidine (9); IR: 3500, 3350, 1640, 1540, 1460, 1390, 1370, 1118, 895 cm^{-1}; mass spectrum: M^+, m/e 140 (intensity 7), 139 (25), 125 (100), 108 (22), 59 (28), and 55 (29).

(e) Reaction of N-Methyldiallylamine (MDAA) with ABIB

A mixture of MDAA (7.6 g, 68 mmoles), HCl (2.4 g, 64 mmoles), and ABIB (5.6 g, 34 mmoles) in ethanol (30 ml) was treated as described in Reaction (a). The neutral fractions contained IBN (3.8 mmoles), EIB (4.2 mmoles), and TMSN (12 mmoles). The basic fraction contained unchanged MDAA (>20 mmoles), and GLC analysis showed essentially only one other elutable component. This was obtained as a fraction, bp, 68°C/0.3 mm (0.93 g), on distillation of the bases, together with DII (0.1 g), subliming ~120°C/0.1 mm, leaving a polymeric high-boiling residue (2.4 g).

The volatile base was identified as the aminoketone (16b), 2,6,6-trimethyl-cis-perhydro-5-isoindolone (5.2 mmoles); IR: C=O, 1708 cm^{-1}; H^1 NMR: $(CH_3)_2C$, singlet, δ 1.09; CH_3N, singlet, δ2.49; the ^{13}C NMR spectrum is described in a later paper [7]; mass spectrum: M^+, m/e 181 (intensity 13), 108 (13), 95 (42), 82 (36), 68 (17), 57 (100), and 42 (53). Hydrochloride, mp, 175°C. Calculated for $C_{11}H_{20}ClNO$: C, 60.7; H, 9.3; N, 6.4; found: C, 60.3; H, 8.8; N, 6.6. Picrate, mp, 187-188°C. Calculated for $C_{17}H_{22}N_4O_8$: C, 49.8; H, 5.4; N, 13.7; found: C, 50.0; H, 5.6; N, 13.5.

Reaction between the aminoketone (100 mg) in tetrahydrofuran (1 ml) and D_2O (0.5 ml) containing NaOD (50 mg) at room temperature for 14 days resulted in the partial exchange of 2 protons; negligible exchange was observed after only 24 hr reaction time.

Attempts to form a benzylidene derivative by reaction of the aminoketone (100 mg) with benzaldehyde (180 mg) in methanol (6 ml) containing 20% aqueous NaOH (1.5 ml) at room temperature were unsuccessful; no reaction was observed when refluxing methanolic $NaOCH_3$ was used as catalyst. Only a small quantity of amphoteric amino-oximinoketone was obtained in the reaction between the aminoketone (100 mg) in methanol (4 ml), butyl nitrite (65 μl), and 10.5 M hydrochloric acid (0.1 ml) at 4°C for 48 hr, the bulk of the aminoketone being recovered unchanged.

The aminoketone (1 g) was reduced by a Wolff-Kischner procedure, the product of the reaction with hydrazine hydrate (2 ml) in ethanol (15 ml) being slowly added to a solution of KOH (2 g) in diethylene glycol maintained at 200-210°C, and the amine recovered from the distillate. The amine identified as 2,5,5-trimethyl-cis-perhydroisoindole (23b); mass spectrum: M^+, m/e 166 (intensity 2), 152 (3), 80(7), 67 (6), 57 (100), and 42 (32); NMR spectrum: $(CH_3)_2C$, δ 0.88, 0.90, CH_3N, δ 2.35. Picrate, mp, 176-179°C. Calculated for $C_{17}H_{24}N_4O_7$: C, 51.5; H, 6.1; N, 14.1; found: C, 51.2; H, 6.0; N, 14.4. The intensity of the amine was confirmed by spectroscopic comparison with an authentic specimen synthesized as described below. The ^{13}C NMR spectrum of the amine is reported elsewhere [7].

(f) Synthesis of 2,5,5-Trimethyl-cis-perhydroisoindole

4,5-Dimethyl-cyclohex-4-ene-cis-1,2-dicarboxylic anhydride (11 g), prepared by the reaction of maleic anhydride and 2,3-dimethylbutadiene, was dissolved in aqueous KOH (20 g in 200 ml water), crushed ice (350 g) added, and the mixture stirred vigorously while finely powdered $KMnO_4$ (10.7 g) was added in one portion. The mixture was stirred at 0-4°C for 15 min, then treated with SO_2 until the colour of residual MnO_2 was discharged. The mixture was acidified to pH 2 with conc hydrochloric acid, evacuated to remove excess SO_2, and then extracted once with ether. The aqueous solution was evaporated under vacuum and the residue extracted with ethanol (50 ml). The ethanolic extract was evaporated and the crude 4,5-dimethyl-cis-4,5-dihydroxy-cyclohexane-cis-1,2-dicarboxylic acid (4 g) recrystallized from a small quantity of water, mp, 210°C (dec) (Ref. 16, mp, 213-215°C). The hydroxy-acid was gently refluxed in a mixture of conc sulfuric acid (15 ml) and water (50 ml) for 8 hr, cooled, and then maintained at 4°C for 72 hr. The solid which separated was dissolved in aqueous $NaHCO_3$, the solution extracted with chloroform, and then acidified to yield 5,5-dimethyl-4-ketocyclohexane-1,2-cis-dicarboxylic acid (1.2 g), recrystallized mp, 215°C (dec) [Ref. 16, 224°C (dec)]; IR: C=O, 1725, 1705 cm^{-1}.

The keto-acid (0.6 g) was heated with excess hydrazine hydrate (3 ml) in ethanol (20 ml) on a steam bath for 1 hr. The resultant slurry was mixed with a solution of KOH (3 g) in diethylene glycol (30 ml) and gradually heated to, and then maintained at, 210-220°C) for 3 hr, the ethanol and excess hydrazine hydrate being extracted with ether, acidified, and then extracted again with ether to give 4,4-dimethylcyclohexane-cis-1,2-dicarboxylic acid; IR: C=O, 1708 cm^{-1}. The crude acid was converted to its N-methylimide by heating its methylamine salt at 250°C for 0.5 hr, and then extracting with aqueous $NaHCO_3$ to remove acidic impurities. The N-methylimide (IR: C=O, 1768, 1700 cm^{-1}) was reduced by reaction with a mixture of excess $LiAlH_4$ (400 mg) and refluxing diethyl ether (25 ml) for 8 hr. The amine (200 mg) was recovered after treatment of the reaction mixture with 2N aqueous NaOH (2 ml), and extraction of the ethereal phase with dilute hydrochloric acid. The 2,5,5-trimethyl-cis-perhydroisoindole was spectroscopically identical with the Wolff-Kishner reduction product described in Reaction (e) above, and its picrate, mp, 185°C, had an unchanged mixed mp with that of the "unknown" amine.

(g) Reaction of N-tert-Butyldiallylamine (BuDAA) with ABIB

A mixture of BuDAA (10.4 g, 68 mmoles), HCl (2.4 g, 64 mmoles), ABIB (5.6 g, 34 mmoles), and ethanol (30 ml) was treated as described for Reaction (a). The neutral fractions contained IBN (1.8 mmoles), EIB (2.3 mmoles), and TMSN (12 mmoles). The basic fraction contained unchanged BuDAA (16 mmoles), DII (1 mmoles), and an aminoketone (2.4 g), bp, 80-82°C/0.1 mm. GLC examination of the basic fraction revealed no other significant, elutable components. The aminoketone was identified as 2-tert-butyl-6,6-dimethylperhydro-5-isoindolone (16c, 11 mmoles); IR: C=O, 1701 cm^{-1}; mass spectrum: M^+, m/e 223 (intensity 5), 219 (9), 208 (100), 191 (5), 138 (18), 120 (8), 94 (6), 80 (21), 69 (9), and 41 (11); NMR spectrum: CH_3C, δ 1.07. Picrate, mp, 168°C. Calculated for $C_{20}H_{28}N_4O_8$: C, 53.1; H, 6.2; N, 12.4; found: C, 53.1; H, 6.3; N, 12.3. The ^{13}C NMR spectrum of the aminoketone is reported elsewhere [7].

(h) Reaction of N-ethyldimethallylamine (EtDMA) with ABIB

(1) EtDMA was prepared by the reaction of methallyl chloride (145 g) with a vigorously-stirred solution of ethylamine (36.2) and NaOH (64 g) in water (200 ml), maintained at 0-5°C. The

mixture was stirred overnight at room temperature and then heated at 60°C for 2 hr. The amine was purified by fractional distillation, pure N-ethyl-dimethallylamine being obtained as a fraction, bp, 58°C/15 mm. Picrate, mp, 80°C. Calculated for $C_{16}H_{22}N_4O_7$: C, 50.3; H, 5.8; N, 14.7; found: C, 50.1; H, 5.8; N, 15.0.

(2) A mixture of EtDMA (15.3 g, 100 mmoles), HCl (3.75 g, 100 mmoles), and ABIB (8.2 g, 50 mmoles) in ethanol (50 ml) was treated as described for Reaction (a). The neutral fractions contained IBN (7.3 mmoles), EIB (8.2 mmoles), and TMSN (36 mmoles). GLC analysis of the basic fraction showed the presence of unreacted EtDMA, the aminoketone described below, and a number of minor components. On distillation the basic fraction yielded a DII-containing fraction, bp, 80-100° C/0.1 mm. The DII (1 mmole) was precipitated on dilution of the distillate with petroleum ether, and redistillation of the mother-liquors yielded the aminoketone fraction, bp, 82°C/0.1 mm. The aminoketone was purified by preparative GLC and identified as 2-ethyl-3a,6,6,7a-tetramethyl-perhydro-5-isoindolone (16e); IR: C=O, 1708 cm^{-1}; mass spectrum: M^+, m/e 223 (intensity 28), 208 (24), 163 (9), 134 (11), 126 (21), 124 (36), 105 (33), 71 (100), and 43 (23). Calculated for $C_{14}H_{25}NO$: M^+, m/e 223; $M+1^+/M^+$, 0.160; $M+2^+/M^+$, 0.014; found; $M+1^+/M^+$, 0.163; $M+2^+/M^+$, 0.014. Two protons of the aminoketone could be exchanged with D_2O using the method described for Reaction (e).

(i) Reaction of N-Benzyldiallylamine (BzDAA) with ABIB

A mixture of BzDAA (13.2 g, 71 mmoles), HCl (2.6 g, 71 mmoles), and ABIB (5.6 g, 34 mmoles) in ethanol (30 ml) was treated as described for Reaction (h) above. The basic fraction on distillation yielded a DII-containing fraction bp, 100-140° C/0.1 mm. After removal of the DII (1 mmole) and redistillation, the major component, 2-benzyl-6,6-dimethylperhydro-5-isoindolone (16d), was obtained as a fraction bp, 132° C/0.1 mm; IR: C=O, 1710 cm^{-1}; mass spectrum: M^+, m/e 257 (intensity 13), 187 (26), 183 (35), 171 (18), 170 (18), 168 (38), 154 (15), 146 (16), 110 (22), 106 (43), 96 (21), and 91 (100). Calculated for $C_{17}H_{23}NO$: M^+, m/e 257; $M+1^+/M^+$, 0.190; $M+2^+/M^+$, 0.190; found: $M+1^+/M^+$, 0.190; $M+2^+/M^+$, 0.020; NMR spectrum: Ph, δ7.35; $PhCH_2$, δ3.62; $(CH_3)_2C$, δ1.10.

(j) Reaction of Triallylamine (TAA) with ABIB

A mixture of TAA (9.3 g, 68 mmoles), HCl (2.4 g, 64 mmoles), and ABIB (5.6 g, 34 mmoles) in ethanol (30 ml) was heated at 60°C in a N_2 atmosphere for 72 hr. The ethanolic product, a mobile

solution, partially gelled after exposure to air and attempted distillation to remove the solvent. The ethanol was removed by vacuum evaporation at room temperature and the basic components separated as described for Reaction (a). The basic fraction contained negligible residual TAA, and only one GLC elutable component. This was obtained as a fraction (150 mg), bp, 70°C/0.3 mm, and identified as 2-allyl-6,6-dimethylperhydro-5-isoindolone (16f); IR: C=O, 1708 cm^{-1}; $CH=CH_2$, 925 cm^{-1}; NMR: $C=CH_2$, δ5.00, 5.23; C=CH, δ ~5.9; $C=C-CH_2N$, δ3.10; $(CH_3)_2C$, δ1.08; mass spectrum: M^+, m/e 207 (intensity 100), 192 (33), 180 (98), 166 (26), 151 (12), 134 (15), 121 (96), 108 (77), 83 (36), 70 (26), and 58 (25). Picrate, mp, 126-128°C. Calculated for $C_{19}H_{24}N_4O_8$: C, 52.3; H, 5.5; N, 12.8; found: C, 52.4; H, 5.7; N, 12.9.

(k) Polymerization of N-Methyldiallylamine (MDAA) using ABIB

A mixture of MDAA (20 g, 210 mmoles), HCl (8.4 g, 230 mmoles), and ABIB (2 g, 12 mmoles) in ethanol (75 ml), plus tri-n-propylamine (2 g, 14 mmoles) as an internal reference, was heated at 75°C under reflux in a N_2 atmosphere. The reaction mixture was sampled at intervals over a period of 23 hr, at which time 32% of the MDAA had reacted. The basic fractions from each of the samples were examined using gel permeation chromatography and were found to have an essentially-invariant molecular weight distribution, with average molecular weight of ~600 relative to polystyrene standards. The various neutral products and the aminoketone described in Reaction (e) were also found in the reaction products. Repetition of the reaction with the addition of hydroquinone resulted in a negligible yield of polymer.

(l) Reaction of MDAA with ABIB in Basic Media

(1) A solution of MDAA (7.5 g, 66 mmoles) and ABIB (5.6 g, 34 mmoles) in ethanol (30 ml) was heated under a N_2 atmosphere for 72 hr. GLC analysis of the reaction mixture showed the presence of unchanged MDAA, IBN, TMSN, and the 2,6,6-trimethylperhydro-5-isoindolone, together with several minor, unidentified components.

(2) The reaction was repeated using sodium-dried benzene (30 ml) as solvent. The reaction mixture was examined by GLC, then acidified with dilute sulfuric acid and analyzed as described for Reaction (e). The neutral fraction contained IBN (3 mmoles) and TMSN (18 mmoles), together with several unidentified components. The 2,6,6-trimethylperhydro-5-isoindolone was not evident in the untreated reaction products. However, a compound was observed

which had a 7% shorter retention time, and which was converted to the aminoketone on treatment with dilute acid. Both the aminoketone and its presumed precursor were observed in the reaction products when undried benzene was used as solvent.

(3) Reaction (2) was repeated with the addition of di-n-butyl disulfide (3.6 g) to the reagent mixture. The products contained the aminoketone precursor in an amount comparable to that observed in Reaction (2). There was no measurable utilization of the disulfide, and no significant amounts of additional by-products were detected using GLC, although the fetid basic fraction obviously contained sulfur derivatives.

ABBREVIATION

ABIA	2,2'-Azobisisobutyramidine dihydrochloride
ABIB	2,2'-Azobisisobutyronitrile
APR	Amidinoisopropyl radical
BuDAA	N-tert-butyldiallylamine
BzDAA	N-Benzyldiallylamine
CPR	Cyanoisopropyl radical
DII	4,4'-Dimethyl-2-isopropyl-2-imidazolin-5-one
DMAA	N,N-Dimethylallylamine
EtDMA	N-Ethyldimethallylamine
EIB	Ethyl isobutyrate
IBN	Isobutyronitrile
MDAA	N-Methyldiallylamine
TAA	Triallylamine
TMSI	Tetramethylsuccinimide
TMAA	N,N,2-Trimethylallylamine
TMSN	Tetramethylsuccinodinitrile

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